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The influence of hydrogeological setting on nitrate fate and transport in Irish and British aquifers and the implications for catchment management

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ABSTRACT

Excess nitrate (NO₃) in groundwater is a significant problem in both Ireland and Britain. This paper presents findings from an Irish study and a British study which both investigate fate and transport of nitrate in groundwater.

The British study, carried out for a water company, quantified the sources and investigated the transport of nitrate in three catchments in rural and semi-urban settings underlain by chalk or sandstone bedrock. The Irish study investigated the influence of hydrogeological setting on nitrate fate in agricultural catchments underlain by bedrock aquifers with contrasting hydrogeological properties.

Both the British and Irish studies highlighted the importance of considering the hydrogeological setting for groundwater quality monitoring and the implementation of contamination mitigation measures. The study in the British catchments highlighted the dominance of agricultural sources of nitrate in both rural and semi-urban settings, the significant lag time for nitrate to reach the abstraction points once applied to the surface, and the implications this has on catchment management interventions. Investigations in the Irish catchments showed that in karstified aquifers nitrate management strategies should focus on the deep groundwater pathways, whereas in catchments underlain by lower permeability aquifers, the focus should be on shallower pathways. Significantly, the study also showed denitrification is occurring in the lower permeability bedrock aquifer. Incorporating these considerations when developing catchment management plans can assist in addressing the impact of agricultural practices on the groundwater quality, reduce long-term costs associated with water treatment and contribute towards achieving the aims of the Water Framework Directive.

INTRODUCTION

Excess nitrate (NO₃) is a global environmental problem which is expected to worsen as a result of factors linked to the increase in human population and the development of growing economies (Erisman et al. 2011). Identifying the sources of nitrate and characterising catchment-scale processes controlling nitrate fate in groundwater is a fundamental consideration when applying interventions to reduce risks posed to water quality.

This paper presents findings from two separate studies. Both studies include catchments which are set in agricultural setting and are associated with groundwater nitrate contamination. The first study was carried out in the UK for Yorkshire Water to investigate the sources of nitrate in rural and semi-urban catchments. The study aimed to inform better focused and more effective actions to reduce nitrate inputs and ultimately to reverse rising trends of nitrate in groundwater abstractions from these aquifers.

The second study was carried out in Ireland to investigate the influence of hydrogeological setting on nitrate fate in Irish agricultural catchments. The study used a field based approach to characterise the dominant processes influencing nitrogen fate in groundwater in catchments underlain by bedrock aquifers with contrasting hydrogeological properties, but having comparable nutrient loads. Findings from this research are presented in Orr et al. (2016) and in the Irish Groundwater Newsletter Issue 54 (2016).

NITRATE SOURCES AND TRANSPORT IN British DUAL POROSITY AQUIFERS

Nitrate concentrations in the unconfined aquifers of Yorkshire have been rising over several decades and many of the public supply sources used by Yorkshire Water now exceed the European Union Drinking Water Directive (98/83/EC) limit of 50 mg/l NO₃ (Figure 1).

Yorkshire Water have always achieved compliance with the Drinking Water Directive through treatment and/or blending. Treatment can be an effective way of removing nitrate but comes with high environmental and economic costs. Treatment plants have short asset lives, require large amounts of power and chemicals and the waste produced can be difficult to dispose of. Capital costs of a nitrate removal plant are approximately £0.5M per Ml/d and subsequent operational costs are typically £5 per kg of N removed. Therefore, catchment management can be both environmentally and economically advantageous compared to conventional treatment technologies or blending, resulting in a more sustainable approach to the problem.

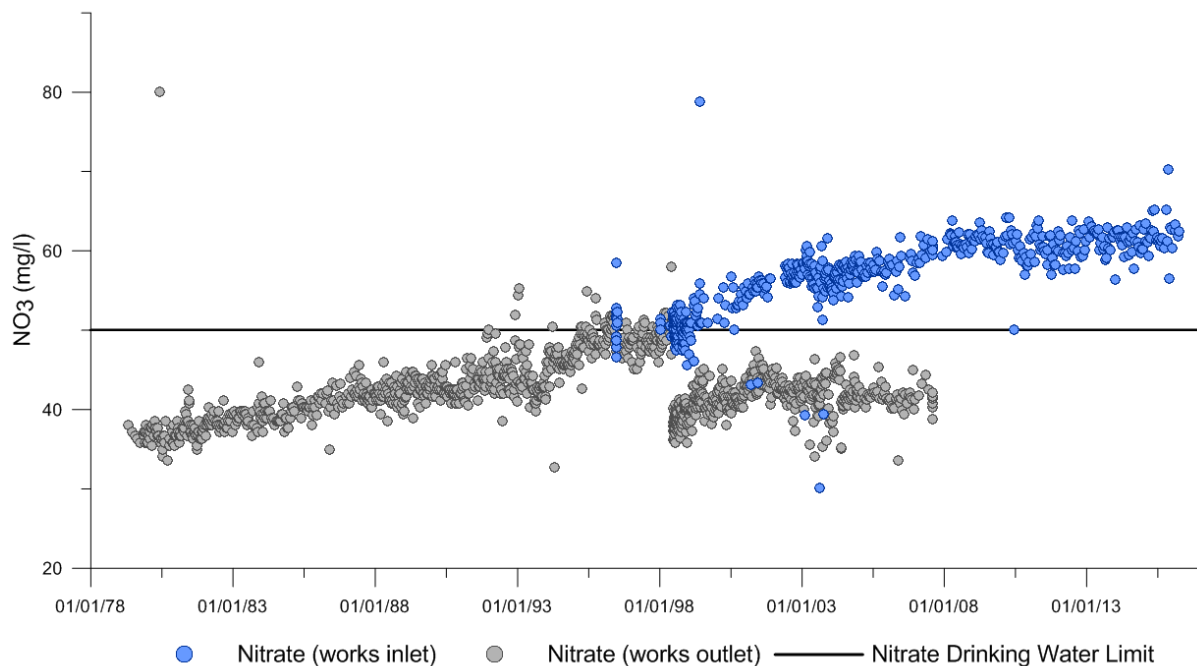


Figure 1 Nitrate concentrations at the works inlet and works outlet at the Kilham abstraction, 1979-2016. The reduction in nitrate concentrations in the works outlet in 1998 was in response to the installation of a treatment works.

Yorkshire Water have highlighted the need to understand the source of nitrate in the raw water abstracted for public water supply to provide a balanced, scientifically robust account of the contributions from non-agricultural and agricultural activities. This improved

understanding of the source of nitrate will help inform water resource managers and farmers on effective catchment management solutions and inform decisions on where, when and how catchment management might reduce the rising trends of nitrate concentrations.

The Yorkshire Water abstractions are located in the Yorkshire Chalk and Triassic Sherwood Sandstone which are principle aquifers of regional importance. In both aquifers recharges is controlled by the presence of low permeability quaternary deposits. The Yorkshire Chalk is highly heterogeneous as a result of dissolution and karstic development. In the Sherwood Sandstone fissure flow is an important source of improved yields as it drains the inter-granular storage. Permeability layering related to grain size is evident within the sandstone where the coarser grained units transmit more groundwater.

This study has three research and development themes:

1. Source Apportionment (the focus of this study), which aims to gain an understanding of the sources of nitrate and to understand the magnitude of nitrate leaching to groundwater. This will allow better focused and more effective actions to reduce nitrate inputs and ultimately to reverse rising trends and reduce nitrate concentrations.
2. Nitrate Storage Transport and Pathways, which aims to improve the characterisation and understanding of the geology and hydrogeology of the catchments with particular focus on characterising the role of soil and superficial geological deposits and infiltration and recharge mechanisms in controlling nitrate levels in underlying groundwater. This will inform the mechanisms by which the nitrate is transported from the sources to the groundwater abstractions, which are the receptors.
3. Integrated Catchment Management, which aims to identify the appropriate and applicable catchment management approach and intervention measures available based on the findings from R&D theme 1 and 2. The interventions aim to reduce the leaching of nitrate from agricultural land to the underlying groundwater body and ultimately into the Yorkshire Water public water supply abstractions.

PILOT CATCHMENTS

Three pilot study catchments were identified as characterising different settings typical of Yorkshire. The three pilot catchments are:

- Kilham: Yorkshire Chalk bedrock aquifer mostly overlain by thin and/or permeable quaternary deposits and located within a rural setting,
- Pollington and Heck: Sherwood Sandstone bedrock aquifer, which is overlain by both areas of thin and/or permeable quaternary deposits and areas of low permeability quaternary deposits. This catchment is located within a rural setting, and
- Armthorpe: Sherwood Sandstone bedrock aquifer, overlain by made ground in urban areas or in the rural areas of both thin and/or permeable quaternary deposits and low permeability quaternary deposits. Armthorpe was chosen specifically because it is located within a semi-urban setting.

The study identified and quantified the sources of nitrate in each catchment. Sources of nitrate considered included agriculture, sewage sludge spreading, leaking sewers, septic

tanks, mains water, urban land uses, landfills, cemeteries, pollution incidents, licenced discharges to groundwater and precipitation.

Agricultural land use was determined from Agricultural Census data (produced by EDINA at Edinburgh University Data Library and the Department of Environment, Food and Rural Affairs (DEFRA) for England) and field scale land use data (CEH Land Cover[®] plus (LC+) Crops). Nitrogen loading rates from each land use were calculated using the Department for Environment Food and Rural Affairs (DEFRA) Fertiliser Manual (RB209) which details recommendations for calculating fertiliser application rates to crops and grassland. The rate of N leaching below the root zone was calculated for each crop type using the Farmscoper decision support tool. It is an open access tool developed by ADAS Ltd to assess agricultural pollution loads and the impacts of farm mitigation measures on pollution loads.

The Catchment Nitrogen and Phosphorus Loading to Groundwater spreadsheet developed by Entec UK Ltd (2010) was used to calculate the rate of N leaching from non-agricultural sources.

NITRATE SOURCES AND TRANSPORT

Based on the nitrate leaching analysis of each identified potential source, the study found that the main source of nitrate in all three catchments is agriculture. In the rural catchments of Kiham and Heck and Pollington agriculture accounted for >88% of the nitrate leaching to groundwater. In these catchments the remaining nitrate leaching to groundwater was from landfills, septic tanks, precipitation and leaking mains water and sewers. In the semi-urban Armthorpe catchment agriculture accounted for 67% of the nitrate leaching to groundwater. Leaking sewers and landfills also accounted for considerable proportions of nitrate leaching to the groundwater. Other urban sources which contribute nitrate leaching to groundwater in the Armthorpe catchment include leaking mains water, septic tanks and urban parks and recreational areas including golf courses and sports playing fields.

Nitrate concentrations in the abstraction boreholes indicate that the abstraction rate can have an influence on the nitrate concentrations, as higher abstraction rates increase the volume of higher nitrate groundwater entering the boreholes. It is likely that this is due to the increase in the cone of depression resulting in an increase in flow from shallower depths of the aquifer which contain younger higher nitrate waters. Furthermore, boreholes with deeper abstraction zones are associated with lower nitrate concentrations. This indicates a decrease in groundwater nitrate concentrations with depth and therefore abstracting from greater depths yields lower nitrate water.

The study found that while there has generally been a decrease in nitrate leaching to groundwater from agricultural sources since the 1980s, there has been an increase in groundwater nitrate concentrations. The increase in nitrate is likely to be as a result of high nitrate storage in the unsaturated zone and this highlights the potential influence of time lag associated with any proposed intervention implemented in the catchments.

NITRATE FATE AND TRANSPORT IN IRISH FRACURED AQUIFERS

The study in Ireland used a field-based approach to characterise the dominant processes influencing nitrogen concentrations in groundwater in two rural Irish catchments underlain

by bedrock aquifers with contrasting (physical and geochemical) hydrogeological properties, but having comparable nutrient loads (approximately 400 kg N/ha/yr) and thin to no subsoil cover over much of their area.

This research examined the spatial heterogeneity of biogeochemical processes across each catchment and with depth. This was achieved through monitoring well tracer tests and the analysis of chemical and isotopic signatures of groundwater and surface water.

The research focused on two catchments; the Nuenna Catchment which is a well-drained catchment underlain by a regionally productive diffuse karst (Rk_d) pure bedded limestone aquifer, and the Glen Burn Catchment which is a poorly drained catchment underlain by a poorly productive (PI) Silurian greywacke aquifer. While both aquifers are fractured, transmissivity ranges determined from pumping tests at well clusters are much greater in the Nuenna compared to the Glen Burn.

NUENNA

Groundwater transport of nitrate in the Nuenna Catchment is dominated by fracture flow in the deep groundwater where nitrate concentrations are higher than in the shallow groundwater (Figure 2). Relatively little change in NO₃/Cl ratios or nitrate isotopic signature with depth suggest good mixing in the deeper part of the aquifer and that biogeochemical reactions are not a significant factor influencing nitrate fate once the nitrate enters the deeper bedrock (Figure 2).

Nitrification is the dominant biogeochemical process influencing N fate in the aquifer. Hydrochemical and isotopic findings suggest that widespread denitrification is unlikely across the Nuenna Catchment but localised partial nitrification may be intermittently occurring in the shallow groundwater with limited impact on catchment surface water quality (Figures 2 and 3).

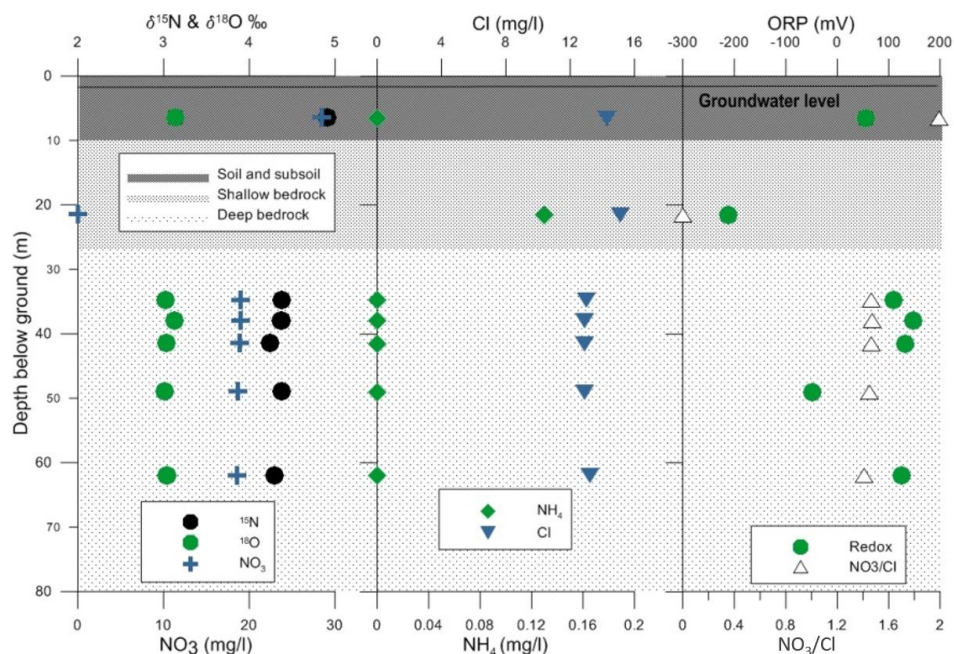


Figure 2 Variation of NO₃, NH₄, Cl, ORP concentrations and NO₃ isotope ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) values with depth in the NU2 cluster, sampled using a packer system and low flow pump, Nuenna Catchment, Co. Kilkenny.

GLEN BURN

In the Glen Burn catchment investigations show that the shallow groundwater is the dominant groundwater pathway for delivering nitrate to aquatic receptors. Water quality and isotopic analyses show that denitrification is likely to be occurring in the bedrock resulting in lower nitrate concentrations with depth (Figures 3 and 4). Water quality data suggest that both autotrophic and heterotrophic denitrification occurs, yet varies spatially across the site according to available electron donors.

Nitrate concentration decreases with depth in the Glen Burn aquifer, which also corresponds to a reduction in the NO_3/Cl ratio (Figure 4). A decrease in NO_3/Cl ratio may indicate dilution from older water. However considering the reduction in oxidation reduction potential (ORP) this would indicate suitable denitrifying conditions. This is supported by the significant enrichment of both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ which indicates denitrification in the bedrock groundwater. More enriched nitrate isotopic values in the deep groundwater compared to the shallow groundwater suggest that nitrate removal through denitrification continues at depth as it infiltrates downwards. This is supported by a general trend across the groundwater samples showing lower groundwater nitrate concentrations contain more enriched $\delta^{15}\text{N}$. Significantly, these values display an enrichment ratio of 1.7 between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Figure 3) which is within the enrichment ratio range of between 1.3 and 2.1 attributed to denitrification (Böttcher et al. 1990; Aravena & Robertson 1998; Fukada et al. 2003)

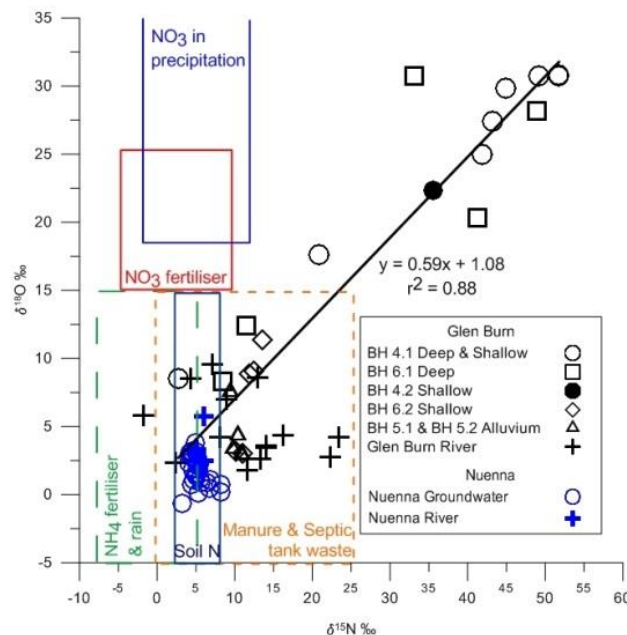


Figure 3 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in groundwater and surface water in the Glen Burn Catchment, Co. Down. Boxes show the range of $\delta^{15}\text{N}$ for manure and septic tank waste, NH_4 fertiliser and soil N, adapted from Kendall (1998).

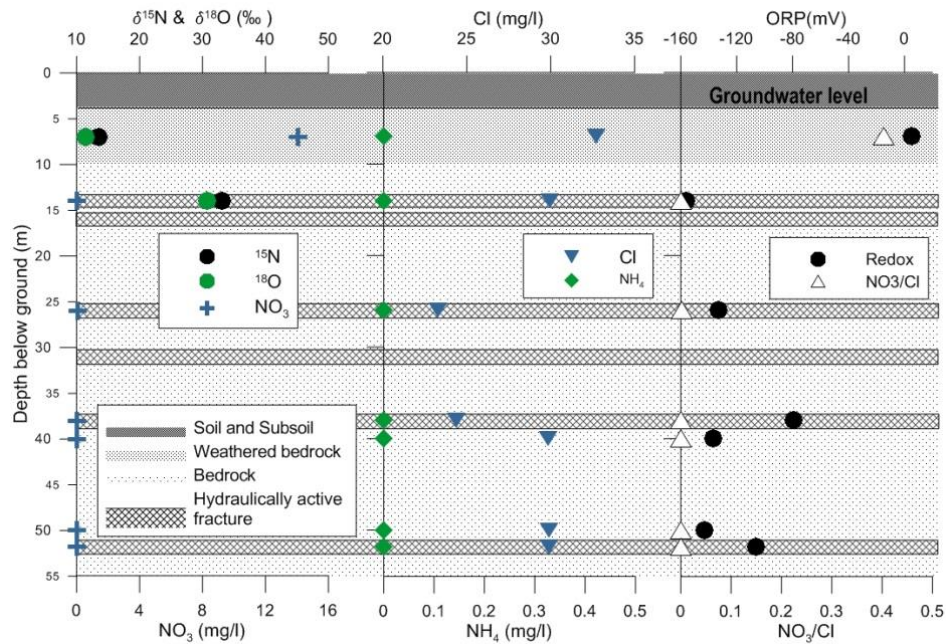


Figure 4 Variation of NO_3^- , NH_4^+ , and ORP concentrations and NO_3^- isotope ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) values with depth in BH6 cluster, sampled using a packer system and low flow pump, Glen Burn, Co. Down.

The findings show that groundwater quality in both the Nuenna and Glen Burn catchments is impacted by contamination. However, the contrasting hydrogeological settings have a significant influence on the dominant biogeochemical processes influencing nitrate fate and transport. The bedrock in both catchments transports groundwater predominantly through fracture flow. However the variation in groundwater discharge via hydraulically active fracture sets with depth and the transmissivity ranges differ considerably in the two catchments investigated. This has considerable influence on the fate and transport of nitrate in the groundwater bodies.

CONCLUSIONS

Both studies highlight the importance of considering the hydrogeological setting for groundwater quality monitoring and the implementation of contamination mitigation measures in catchments. The study in the British catchments highlights the dominance of agricultural sources of nitrate, the lag time for nitrate to reach the abstractions once applied to the surface and the implications this has on catchment management interventions. The study in the Irish catchments shows that in karstified aquifers nitrate management strategies should focus on the role played by deep groundwater pathways and diffuse nitrogen sources, whereas in catchments underlain by lower permeability aquifers, the deep groundwater will be a less significant pathway for nitrate and the focus of such management plans should be on pathways nearer the ground surface. Furthermore, denitrification is evident in the lower permeability bedrock aquifer. Incorporating these considerations when developing catchment management plans can assist in addressing the impact of agricultural practices on the water quality of groundwater bodies and contribute toward achieving the aims of the Water Framework Directive.

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